

CLAIMS

What is claimed:

1. A method of fabricating a semiconductor device, having a reduced-oxygen copper-zinc alloy (Cu-Zn) thin film formed on a copper (Cu) surface by electroplating the Cu surface in a chemical solution, comprising the steps of:
 providing a semiconductor substrate having a Cu surface;
 providing a chemical solution;
 electroplating the Cu surface in the chemical solution, thereby forming a Cu-Zn alloy thin film on the Cu surface;
 rinsing the Cu-Zn alloy thin film in a solvent;
 drying the Cu-Zn alloy thin film under a gaseous flow;
 annealing the Cu-Zn alloy thin film formed on the Cu surface, thereby forming a reduced-oxygen Cu-Zn alloy thin film; and
 completing formation of the semiconductor device.
2. A method, as recited in Claim 1,
 wherein the chemical solution is nontoxic and aqueous, and
 wherein the chemical solution comprises:
 at least one zinc (Zn) ion source for providing a plurality of Zn ions;
 at least one copper (Cu) ion source for providing a plurality of Cu ions;
 at least one complexing agent for complexing the plurality of Cu ions;
 at least one pH adjuster;
 at least one wetting agent for stabilizing the chemical solution, all being dissolved in a volume of deionized (DI) water.

3. A method, as recited in Claim 2,

wherein the at least one zinc (Zn) ion source comprises at least one zinc salt

selected from a group consisting essentially of zinc acetate ($(\text{CH}_3\text{CO}_2)_2\text{Zn}$), zinc bromide (ZnBr_2), zinc carbonate hydroxide ($\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$), zinc dichloride (ZnCl_2), zinc citrate ($(\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2)_2\text{Zn}_3$), zinc iodide (ZnI_2), zinc L-lactate ($(\text{CH}_3\text{CH}(\text{OH})\text{CO}_2)_2\text{Zn}$), zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), zinc stearate ($(\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2)_2\text{Zn}$), zinc sulfate (ZnSO_4), zinc sulfide (ZnS), zinc sulfite (ZnSO_3), and their hydrates.

4. A method, as recited in Claim 2,

wherein the at least one copper (Cu) ion source comprises at least one copper salt

selected from a group consisting essentially of copper(I) acetate ($\text{CH}_3\text{CO}_2\text{Cu}$), copper(II) acetate ($(\text{CH}_3\text{CO}_2)_2\text{Cu}$), copper(I) bromide (CuBr), copper(II) bromide (CuBr_2), copper(II) hydroxide ($\text{Cu}(\text{OH})_2$), copper(II) hydroxide phosphate ($\text{Cu}_2(\text{OH})\text{PO}_4$), copper(I) iodide (CuI), copper(II) nitrate ($(\text{CuNO}_3)_2$), copper(II) sulfate (CuSO_4), copper(I) sulfide (Cu_2S), copper(II) sulfide (CuS), copper(II) tartrate ($(\text{CH}(\text{OH})\text{CO}_2)_2\text{Cu}$), and their hydrates.

5. A method, as recited in Claim 1,

wherein said electroplating step comprises using an electroplating apparatus, and wherein said electroplating apparatus comprises:

- (a) a cathode-wafer;
- (b) an anode;
- (c) an electroplating vessel; and
- (d) a voltage source.

6. A method, as recited in Claim 5,
wherein the cathode-wafer comprises the Cu surface, and
wherein the anode comprises at least one material selected from a group consisting
essentially of copper (Cu), a copper-platinum alloy (Cu-Pt), titanium (Ti),
platinum (Pt), a titanium-platinum alloy (Ti-Pt), an anodized copper-zinc
alloy (Cu-Zn, i.e., brass), a platinized titanium (Pt/Ti), and a platinized
copper-zinc (Pt/Cu-Zn, i.e., platinized brass).
7. A method, as recited in Claim 6, further comprising the step of anodizing the
copper-zinc alloy to form a thin oxide film in situ using the chemical solution prior
to said electroplating step.
8. A method, as recited in Claim 5,
wherein said electroplating comprises a plating condition selected from a group
consisting essentially of a direct voltage in the range of approximately 1 V to
approximately 4 V and a direct current in the range of approximately 0.01 A
to approximately 0.2 A.
9. A method, as recited in Claim 5,
wherein the Zn-doping in the reduced-oxygen Cu-Zn alloy thin film is controllable
by varying at least one electroplating condition selected from a group
consisting essentially of:
increasing the at least one zinc (Zn) ion source concentration, thereby slowly
increasing said Zn-doping;
increasing the at least one copper (Cu) ion source concentration, thereby slowly
decreasing said Zn-doping;
increasing the solution flow rate increases Zn-doping,
thereby increasing the pH decreases cathodic efficiency with respect to Zn,
and
thereby decreasing said Zn-doping;
increasing the electroplating duration, thereby slowly decreasing said Zn-doping;
using a Cu anode, thereby decreasing said Zn-doping;

- 15 using a brass anode, thereby increasing said Zn-doping;
increasing the voltage, thereby increasing the Zn-doping; and
increasing the current, thereby increasing the Zn-doping.
10. A method, as recited in Claim 1,
wherein the annealing step is performed in a temperature range of approximately
150°C to approximately 450°C, and
wherein the annealing step is performed for a duration range of approximately 0.5
5 minutes to approximately 60 minutes.
11. A semiconductor device, having a reduced-oxygen copper-zinc alloy (Cu-Zn) thin
film formed on a copper (Cu) surface by electroplating the Cu surface in a chemical
solution, fabricated by a method comprising the steps of:
providing a semiconductor substrate having a Cu surface;
providing a chemical solution;
electroplating the Cu surface in the chemical solution, thereby forming a Cu-Zn
alloy thin film on the Cu surface;
rinsing the Cu-Zn alloy thin film in a solvent;
drying the Cu-Zn alloy thin film under a gaseous flow;
annealing the Cu-Zn alloy thin film formed on the Cu surface, thereby forming a
reduced-oxygen Cu-Zn alloy thin film; and
completing formation of the semiconductor device.
12. A device, as recited in Claim 11,
wherein the chemical solution is nontoxic and aqueous, and
wherein the chemical solution comprises:
at least one zinc (Zn) ion source for providing a plurality of Zn ions;
5 at least one copper (Cu) ion source for providing a plurality of Cu ions;
at least one complexing agent for complexing the plurality of Cu ions;
at least one pH adjuster;
at least one wetting agent for stabilizing the chemical solution, all being
dissolved in a volume of deionized (DI) water.

13. A device, as recited in Claim 12,

wherein the at least one zinc (Zn) ion source comprises at least one zinc salt

selected from a group consisting essentially of zinc acetate $((\text{CH}_3\text{CO}_2)_2\text{Zn})$, zinc bromide (ZnBr_2) , zinc carbonate hydroxide $(\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2)$, zinc dichloride (ZnCl_2) , zinc citrate $((\text{O}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2)\text{CH}_2\text{CO}_2)_2\text{Zn}_3)$, zinc iodide (ZnI_2) , zinc L-lactate $((\text{CH}_3\text{CH}(\text{OH})\text{CO}_2)_2\text{Zn})$, zinc nitrate $(\text{Zn}(\text{NO}_3)_2)$, zinc stearate $((\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2)_2\text{Zn})$, zinc sulfate (ZnSO_4) , zinc sulfide (ZnS) , zinc sulfite (ZnSO_3) , and their hydrates.

14. A device, as recited in Claim 12,

wherein the at least one copper (Cu) ion source comprises at least one copper salt

selected from a group consisting essentially of copper(I) acetate $(\text{CH}_3\text{CO}_2\text{Cu})$, copper(II) acetate $((\text{CH}_3\text{CO}_2)_2\text{Cu})$, copper(I) bromide (CuBr) , copper(II) bromide (CuBr_2) , copper(II) hydroxide $(\text{Cu}(\text{OH})_2)$, copper(II) hydroxide phosphate $(\text{Cu}_2(\text{OH})\text{PO}_4)$, copper(I) iodide (CuI) , copper(II) nitrate hydrate $((\text{CuNO}_3)_2)$, copper(II) sulfate (CuSO_4) , copper(I) sulfide (Cu_2S) , copper(II) sulfide (CuS) , copper(II) tartrate $((\text{CH}(\text{OH})\text{CO}_2)_2\text{Cu})$, and their hydrates.

15. A device, as recited in Claim 11,

wherein said electroplating step of said method comprises using an electroplating apparatus, and

wherein said electroplating apparatus comprises:

- (a) a cathode-wafer;
- (b) an anode;
- (c) an electroplating vessel; and
- (d) a voltage source.

16. A device, as recited in Claim 15,
wherein the cathode-wafer comprises the Cu surface, and
wherein the anode comprises at least one material selected from a group consisting
essentially of copper (Cu), a copper-platinum alloy (Cu-Pt), titanium (Ti),
platinum (Pt), a titanium-platinum alloy (Ti-Pt), an anodized copper-zinc
alloy (Cu-Zn, i.e., brass), a platinized titanium (Pt/Ti), and a platinized
copper-zinc (Pt/Cu-Zn, i.e., platinized brass).
17. A device, as recited in Claim 16,
wherein said method further comprises the step of anodizing the copper-zinc alloy
to form a thin oxide film in situ using the chemical solution prior to said
electroplating step.
18. A device, as recited in Claim 15,
wherein said electroplating comprises a plating condition selected from a group
consisting essentially of a direct voltage in the range of approximately 1 V to
approximately 4 V and a direct current in the range of approximately 0.01 A
to approximately 0.2 A.
19. A device, as recited in Claim 15,
wherein the Zn-doping (i.e., Zn content) in the reduced-oxygen Cu-Zn alloy thin
film is controllable by varying at least one electroplating condition selected
from a group consisting essentially of:
increasing the at least one zinc (Zn) ion source concentration, thereby slowly
increasing said Zn-doping;
increasing the at least one copper (Cu) ion source concentration, thereby slowly
decreasing said Zn-doping;
increasing the solution flow rate increases Zn-doping,
thereby increasing the pH decreases cathodic efficiency with respect to Zn,
and
thereby decreasing said Zn-doping;
increasing the electroplating duration, thereby slowly decreasing said Zn-doping;
using a Cu anode, thereby decreasing said Zn-doping;

15 using a brass anode, thereby increasing said Zn-doping;
increasing the voltage, thereby increasing the Zn-doping; and
increasing the current, thereby increasing the Zn-doping.

20. A semiconductor device, having a reduced-oxygen copper-zinc alloy (Cu-Zn) thin film formed on a copper (Cu) surface, comprising:
a semiconductor substrate having at least one Cu surface formed thereon; and
a reduced-oxygen Cu-Zn alloy thin film formed, by electroplating, and disposed on
5 the at least one Cu surface,
wherein the reduced-oxygen Cu-Zn alloy thin film is formed by annealing a Cu-Zn alloy thin film in a temperature range of approximately 150°C to approximately 450°C, and
wherein the reduced-oxygen Cu-Zn alloy thin film is formed by annealing a Cu-Zn alloy thin film for a duration range of approximately 0.5 minutes to approximately 60 minutes.